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# Synthesis and thermotropic properties of novel double-chained quaternary ammonium chlorides with symmetric and asymmetric hydrocarbon chain length

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### ABSTRACT

A series of novel double-chained quaternary ammonium chlorides with symmetrical and asymmetrical hydrocarbon chain length  $R_1$ –O–CH<sub>2</sub>–CH(OH)–CH<sub>2</sub>–N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>–R<sub>2</sub>·Cl<sup>-</sup> (R<sub>1</sub>, R<sub>2</sub>: C<sub>12</sub>H<sub>25</sub>, C<sub>14</sub>H<sub>29</sub>, C<sub>16</sub>H<sub>33</sub>) have been synthesized by the reaction of 1-O-alkyl glycidyl ether with *N*,*N*-dimethylalkylamine and *N*,*N*-dimethylalkylamine hydrochloride. Their chemical structures have been characterized through FT-IR, <sup>1</sup>H NMR, MS and elementary analysis. Their thermotropic properties have been examined by differential scanning calorimetry (DSC), polarizing light microscopy (PLM) and X-ray diffraction (XRD). It has been found that the compounds with longer hydrocarbon chain length and being higher asymmetry in hydrocarbon chain length exhibit lower melting point ( $T_m$ ), isotropization temperature ( $T_i$ ) and narrower mesophase temperature range. However, the hydrocarbon chain length and the symmetry in the hydrocarbon chain length have little influence on the type of liquid crystals. All compounds form cholesteric liquid crystal.

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### 1. Introduction

Many amphiphilic molecules exhibit thermotropic liquid crystalline behavior upon heating from solids or cooling from liquid. It has been known that certain ionic soaps, some cationic surfactants, most carbohydrate derivatives, a few zwitterionic and poly(oxyethylene) nonionic surfactant and some catanionic surfactants exhibit thermotropic phase behavior [1-12]. The type of liquid-crystalline phases exhibited by these compounds depends on an interplay of the length and number of lipophilic chains, the nature of the polar heads. Some single-chained quaternary ammonium salts display thermotropic phase behavior. Some doublechained quaternary ammonium salts also exhibit thermotropic liquid crystalline behavior [13-16]. Arkas et al. [14] has reported that N-cyanoalkyl(from methyl to hexyl)-N-alkyl(from dodecyl to octadecyl)-N,N-dimethylammonium bromides display smectic A phase. Alami et al. [15] has found that N,N-dialkyl-N,N-dimethylammonium bromides with alkyl chains from dodecyl to octadecyl show smectic T phase. Everaars et al. [16] has investigated thermotropic liquid crystalline behavior of a series of isomeric doublechained guaternary ammonium salts. Some double-chained guaternary ammonium salts tend to self-associate in water to form vesicles, and lyotropic liquid crystals. Didodecyldimethylammonium bromide (DDAB) aggregates extensively in aqueous solutions into stable bilayer structures, which further form vesicles and lamellae [17]. It can also form four microstructures such as an isotropic micellar phase, a metastable  $L_3$  sponge phase, a dispersion of pure crystallites of lamellar phase in an isotropic phase, and a pure lamellar phase  $L_{\alpha}$  form upon increasing its concentration in water [18]. Dioctadecyldimethylammonium chloride (DODAC) [19] and Some double-chained quaternary ammonium bromides containing acyl hydrophobic chains [20,21] can form vesicles in water.

Previous studies suggest that thermotropic properties of double-chained quaternary ammonium salts strongly depend on the structure and length of lipophilic chains, the nature of the counter ions. More studies of these compounds will lead to better understanding of their thermotropic phase behavior. In this paper, a new series of double-chained quaternary ammonium chlorides with symmetrical and asymmetrical hydrocarbon chain length, N-(3-alkoxyl-2-hydroxy)propyl-N-alkyl dimethylammonium chloride  $R_1$ –O–CH<sub>2</sub>–CH(OH)–CH<sub>2</sub>–N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>– $R_2$ ·Cl<sup>-</sup> ( $R_1$ ,  $R_2$ :  $C_{12}H_{25}$ ,  $C_{14}H_{29}$ ,  $C_{16}H_{33}$ ), has been synthesized (see Scheme 1). In previous studies, bromide has been chosen as counter-ion, mainly because the bromides are easier to synthesize. In this study, chloride is chosen as counter-ion. The thermotropic properties of these novel double-chained guaternary ammonium chlorides have been investigated by DSC, PLM, and XRD. The purpose of this study is to investigate the relationship between structure and property by varying the hydrocarbon chain length and the symmetry in hydrocarbon chain length. Based on the obtained results, some conclusions as to the length of the hydrocarbon chain, the symmetry in the hydrocarbon chain, and mesophase formation will be present.





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$$R_{1}OH + \underbrace{\bigcirc}_{O}CH_{2}CI \xrightarrow{\mathbf{n}-Bu_{4}N^{+}Br}_{N aOH/hexare} \underbrace{\bigcirc}_{O}CH_{2}OR_{1} \xrightarrow{R_{2}N(CH_{3})_{2}/R_{2}N(CH_{3})_{2}.HCl}_{ethanol, 24h} R_{1}O-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH$$

Scheme 1. Synthetic route of symmetrical and asymmetrical double-chained quaternary ammonium chlorides.

### 2. Experimental and methods

### 2.1. Materials

Dodecanol (>98%), tetradecanol (>98%) and hexadecanol (>98%) were purchased from China Pharamactical Corporation (Shanghai, China). *N*,*N*-dimethyldodecylamine (>98%), *N*,*N*-dimethyltetrade-cylamine (>98%) and *N*,*N*-dimethylhexadecylamine (>98%) were purchased from Shanghai Jingwei Chemical Company (Shanghai, China). Epichlorohydrin, sodium hydroxide, hydrochloric acid, chlorosulfonic acid and other solvents were all analytical grade.

### 2.2. Synthesis of long-chain 1-O-alkyl glyceryl ethers

Long-chain 1-O-alkyl glycidyl ether was prepared by the reaction of long-chained fatty alcohol with epichlorohydrin under phase-transfer catalytic condition according to the literature [22].

### 2.3. Synthesis of double-chained quaternary ammonium salts

A mixture of 1-O-alkyl glyceryl ether (0.1 mol), N,N-dimethylalkylamine (0.05 mol) and its hydrochloride (0.1 mol) [23] in isopropanol (50 mL) was heated to reflux for 24 h. After the solvent was evaporated under reduced pressure, the residue was recrystallized several times from acetonitrile and dried under reduced pressure to give the final products as white crystals. Their yields were 90%. Their chemical structures and purities were confirmed by <sup>1</sup>H NMR (Advance 600, Bruker), MS (API 4000) and elemental analysis (Perkin-Elmer 2400). These double-chained guaternary ammonium chlorides  $R_1$ -O-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>-R<sub>2</sub>·Cl<sup>-</sup> (R<sub>1</sub>, R<sub>2</sub>:  $C_{12}H_{25}$ ,  $C_{14}H_{29}$ ,  $C_{16}H_{33}$ ) are abbreviated as  $G_{12}A_{12}C$  ( $R_1$ ,  $R_2 = C_{12}H_{25}$ ),  $G_{14}A_{14}C$  (R<sub>1</sub>, R<sub>2</sub> =  $C_{14}H_{29}$ ),  $G_{16}A_{16}C$  (R<sub>1</sub>, R<sub>2</sub> =  $C_{16}H_{33}$ ),  $G_{14}A_{12}C$  $(R_1 = C_{14}H_{29}, R_2 = C_{12}H_{25}), G_{16}A_{12}C (R_1 = C_{16}H_{33}, R_2 = C_{12}H_{25}),$  $G_{12}A_{14}C$  ( $R_1 = C_{12}H_{25}$ ,  $R_2 = C_{14}H_{29}$ ),  $G_{12}A_{16}C$  ( $R_1 = C_{12}H_{25}$ ,  $R_2 = C_{14}H_{29}$ )  $C_{16}H_{33}$ ),  $G_{14}A_{16}C$  ( $R_1 = C_{14}H_{29}$ ,  $R_2 = C_{16}H_{33}$ ),  $G_{16}A_{14}C$  ( $R_1 = C_{16}H_{33}$ ,  $R_2 = C_{14}H_{29}$ ).

 $\begin{array}{l} G_{12}A_{12}\text{C: }^{1}\text{H NMR (CDCl}_{3}, \text{TMS, in ppm): } 0.86 (t, 6H, 2C\textbf{H}_{3}-), \\ 1.23-1.32 (m, 36H, 2-(C\textbf{H}_{2})_{9}-), 1.50 (t, 2H, N^{+}-CH_{2}-C\textbf{H}_{2}-), 1.70 \\ (t, 2H, O-CH_{2}-C\textbf{H}_{2}-), 3.33-3.43 (m, 10H, 2C\textbf{H}_{3}-N^{+}, N^{+}-C\textbf{H}_{2}-CH_{2}-, \\ O-C\textbf{H}_{2}-CH_{2}-), 3.52-3.57 [m, 4H, -CH(OH)-C\textbf{H}_{2}-N^{+}, O-C\textbf{H}_{2}-CH(OH)-], 4.38 [m, 1H, -C\textbf{H}(OH)-]. Elemental analysis: calcd. (%) \\ \text{for } C_{29}H_{62}NO_{2}Cl (492.26): C, 70.76; H, 12.69; N, 2.85; \\ \text{found: Classes}, H, 12.44; N, 2.70\%. MS: signal at = 456.9 (m/z) [M-Cl^{-}]^{+}. \end{array}$ 

 $G_{14}A_{14}C$ : <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, in ppm): 0.88 (t, 6H, 2CH<sub>3</sub>–), 1.26–1.35 (m, 44H, 2–(CH<sub>2</sub>)<sub>11</sub>–), 1.52(t, 2H, N<sup>+</sup>–CH<sub>2</sub>–CH<sub>2</sub>–), 1.73 (t, 2H, O–CH<sub>2</sub>–CH<sub>2</sub>–), 3.38–3.47 (m, 10H, 2CH<sub>3</sub>–N<sup>+</sup>, N<sup>+</sup>–CH<sub>2</sub>–CH<sub>2</sub>–, O–CH<sub>2</sub>–CH<sub>2</sub>–), 3.54–3.55 [m, 2H, –CH(OH)–CH<sub>2</sub>–N<sup>+</sup>], 3.58–3.62 [m, 2H, O–CH<sub>2</sub>–CH(OH)–], 4.46 [m, 1H, –CH(OH)–]. Elemental analysis: calcd. (%) for  $C_{33}H_{70}NO_2Cl$  (548.36): C, 72.28; H, 12.87; N, 2.55; found: C, 71.65; H, 12.64; N, 2.39%. MS: signal at = 513.0 (*m/z*) [M–Cl<sup>–</sup>]<sup>+</sup>.

 $G_{16}A_{16}C$ : <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, in ppm): 0.88 (t, 6H, 2CH<sub>3</sub>–), 1.25–1.35 (m, 52H, 2–(CH<sub>2</sub>)<sub>13</sub>–), 1.52 (t, 2H, N<sup>+</sup>–CH<sub>2</sub>–CH<sub>2</sub>–), 1.74 (t, 2H, O–CH<sub>2</sub>–CH<sub>2</sub>–), 3.36 (s, 3H, CH<sub>3</sub>–N<sup>+</sup>), 3.39–3.43 (m, 6H, CH<sub>3</sub>–N<sup>+</sup>, N<sup>+</sup>–CH<sub>2</sub>–CH<sub>2</sub>–, O–CH<sub>2/2</sub>–CH<sub>2</sub>–), 3.47–3.53 [m, 3H, – CH(OH)–CH<sub>2</sub>–N<sup>+</sup>, O–CH<sub>2/2</sub>–CH<sub>2</sub>–], 3.58–3.64 [m, 2H, O–CH<sub>2</sub>– CH(OH)–], 4.48 [m, 1H, –CH(OH)–]. Elemental analysis: calcd. (%) for  $C_{37}H_{78}NO_2Cl$  (604.47): C, 73.52; H, 13.00; N 2.32; found: C, 73.66; H, 12.77; N, 2.21%. MS: signal at = 569.0 (m/z) [M-Cl<sup>-</sup>]<sup>+</sup>.

 $G_{14}A_{12}C$ : <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, in ppm): 0.88 (t, 6H, 2CH<sub>3</sub>–), 1.26–1.36 [m, 40H, -(CH<sub>2</sub>)<sub>9</sub>–, -(CH<sub>2</sub>)<sub>11</sub>–], 1.51 (t, 2H, N<sup>+</sup>–CH<sub>2</sub>– CH<sub>2</sub>–), 1.73 (t, 2H, O–CH<sub>2</sub>–CH<sub>2</sub>–), 3.36–3.46 (m, 10H, 2CH<sub>3</sub>–N<sup>+</sup>, N<sup>+</sup>–CH<sub>2</sub>–CH<sub>2</sub>–, O–CH<sub>2</sub>–CH<sub>2</sub>–), 3.55–3.59 [m, 4H, –CH(OH)–CH<sub>2</sub>– N<sup>+</sup>, O–CH<sub>2</sub>–CH(OH)–], 4.44 [m, 1H, –CH(OH)–]. Elemental analysis: calcd. (%) for C<sub>31</sub>H<sub>66</sub>NO<sub>2</sub>C (520.31): C, 71.56; H, 12.78; N, 2.69; found: C, 71.09; H, 12.54, N, 2.52%. MS: signal at = 484.9 (*m/z*) [M–Cl<sup>–</sup>]<sup>+</sup>.

 $\begin{array}{l} G_{16}A_{12}\text{C: }^{1}\text{H NMR (CDCl_3, TMS, in ppm): } 0.89 \ (t, 6H, 2C\textbf{H}_{3}-), \\ 1.27-1.37 \ [m, 44H, -(C\textbf{H}_{2})_{9}-, -(C\textbf{H}_{2})_{13}-], 1.52 \ (t, 2H, N^{+}-CH_{2}-C\textbf{H}_{2}-), 1.75 \ (t, 2H, O-CH_{2}-C\textbf{H}_{2}-) \ 3.39-3.49 \ (m, 10H, 2C\textbf{H}_{3}-N^{+}, \\ N^{+}-C\textbf{H}_{2}-CH_{2}-, O-C\textbf{H}_{2}-CH_{2}-) \ 3.55-3.61 \ [m, 4H, -CH(OH)-C\textbf{H}_{2}-N^{+}, \\ O-C\textbf{H}_{2}-CH(OH)-], 4.48 \ [m, 1H, -C\textbf{H}(OH)-]. Elemental analysis: calcd. (%) for C_{33}H_{70}NO_{2}Cl \ (548.36): C, 72.28; H, 12.87; N, 2.55; \\ found: C, 72.38; H, 12.61; N, 2.41\%. MS: signal at = 513.0 \ (m/z) \ [M-Cl^{-}]^{+}. \end{array}$ 

 $G_{12}A_{14}C$ : <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, in ppm): 0.88 (t, 6H, 2CH<sub>3</sub>–), 1.26–1.34 [m, 40H, -(CH<sub>2</sub>)<sub>9</sub>–, -(CH<sub>2</sub>)<sub>11</sub>–], 1.51 (t, 2H, N<sup>+</sup>-CH<sub>2</sub>– CH<sub>2</sub>–), 1.72 (t, 2H, O–CH<sub>2</sub>–CH<sub>2</sub>–), 3.35–3.46 (m, 10H, 2CH<sub>3</sub>–N<sup>+</sup>, N<sup>+</sup>-CH<sub>2</sub>–CH<sub>2</sub>–, O–CH<sub>2</sub>–CH<sub>2</sub>–), 3.53–3.59 [m, 4H, –CH(OH)–CH<sub>2</sub>– N<sup>+</sup>, O–CH<sub>2</sub>–CH(OH)–], 4.44 [m, 1H, –CH(OH)–]. Elemental analysis: calcd. (%) for C<sub>31</sub>H<sub>66</sub>NO<sub>2</sub>Cl (520.31): C, 71.56; H, 12.78; N, 2.69; found: C, 71.56; H, 12.51; N, 2.54%. MS: signal at = 484.9 (*m/z*) [M–Cl<sup>–</sup>]<sup>+</sup>.

 $G_{12}A_{16}C$ : <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, in ppm): 0.87 (t, 6H, 2CH<sub>3</sub>–), 1.24–1.33 [m, 44H, -(CH<sub>2</sub>)<sub>9</sub>–, -(CH<sub>2</sub>)<sub>13</sub>–], 1.50 (t, 2H, N<sup>+</sup>-CH<sub>2</sub>– CH<sub>2</sub>–), 1.71 (t, 2H, O-CH<sub>2</sub>–CH<sub>2</sub>–) 3.36–3.45 (m, 10H, 2CH<sub>3</sub>–N<sup>+</sup>, N<sup>+</sup>-CH<sub>2</sub>–CH<sub>2</sub>–, O-CH<sub>2</sub>–CH<sub>2</sub>–), 3.51–3.53 [m, 2H, -CH(OH)–CH<sub>2</sub>– N<sup>+</sup>], 3.55–3.58 [m, 2H, O-CH<sub>2</sub>–CH(OH)–], 4.42 [m, 1H, -CH(OH)– ]. Elemental analysis: calcd. (%) for C<sub>33</sub>H<sub>70</sub>NO<sub>2</sub>Cl (548.36): C, 72.28; H 12.87; N 2.55; found: C, 72.08; H, 12.67; N, 2.37%. MS: signal at = 513.1 (*m/z*) [M–Cl<sup>-</sup>]<sup>+</sup>.

 $G_{14}A_{16}C$ : <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, in ppm): 0.88 (t, 6H, 2CH<sub>3</sub>–), 1.26–1.35 [m, 48H, –(CH<sub>2</sub>)<sub>11</sub>–, –(CH<sub>2</sub>)<sub>13</sub>–], 1.51 (t, 2H, N<sup>+</sup>–CH<sub>2</sub>– CH<sub>2</sub>–), 1.73 (t, 2H, O–CH<sub>2</sub>–CH<sub>2</sub>–), 3.38–3.47 (m, 10H, 2CH<sub>3</sub>–N<sup>+</sup>, N<sup>+</sup>–CH<sub>2</sub>–CH<sub>2</sub>–, O–CH<sub>2</sub>–CH<sub>2</sub>–), 3.53–3.54 [m, 2H, –CH(OH)–CH<sub>2</sub>– N<sup>+</sup>], 3.58–3.60 [m, 2H, O–CH<sub>2</sub>–CH(OH)–], 4.44 [m, 1H, –CH(OH)– ]. Elemental analysis: calcd. (%) for C<sub>35</sub>H<sub>74</sub>NO<sub>2</sub>Cl (576.42): C, 72.93; H, 12.94; N, 2.43; found: C, 72.72; H, 13.30; N, 2.32%. MS: signal at = 541.0 (*m*/*z*) [M–Cl<sup>–</sup>]<sup>+</sup>.

 $G_{16}A_{14}C$ : <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, in ppm): 0.88 (t, 6H, 2CH<sub>3</sub>–), 1.26–1.34 [m, 48H, -(CH<sub>2</sub>)<sub>11</sub>–, -(CH<sub>2</sub>)<sub>13</sub>–], 1.51 (t, 2H, N<sup>+</sup>-CH<sub>2</sub>– CH<sub>2</sub>–), 1.73 (t, 2H, O-CH<sub>2</sub>–CH<sub>2</sub>–) 3.36–3.46 (m, 10H, 2CH<sub>3</sub>–N<sup>+</sup>, N<sup>+</sup>-CH<sub>2</sub>–CH<sub>2</sub>–, O-CH<sub>2</sub>–CH<sub>2</sub>–), 3.52–3.55 [m, 2H, -CH(OH)–CH<sub>2</sub>– N<sup>+</sup>], 3.57–3.60 [m, 2H, O-CH<sub>2</sub>–CH(OH)–], 4.44 [m, 1H, -CH(OH)– ]. Elemental analysis: calcd. (%) for C<sub>35</sub>H<sub>74</sub>NO<sub>2</sub>Cl (576.42): C, 72.93; H, 12.94; N, 2.43; found: C, 72.81; H, 13.27; N, 2.34%. MS: signal at = 541.01 (*m*/*z*) [M–Cl<sup>–</sup>]<sup>+</sup>.

### 2.4. Methods

# 2.4.1. Thermogravimetry (TGA) and differential scanning calorimetry (DSC)

The thermal stability was analyzed by SDT Q600 V8.0 Build 95 heating rate of 10  $^{\circ}$ C/min in nitrogen (50 mL/min). DSC measure-

ments were carried out using a  $822^{e}$  DSC (Mettler Toleodo) equipped with a cryostat cooling system. Heating–cooling cycles were performed at a scanning rate of 5 °C/min. A flow rate of 50 mL of nitrogen was used in DSC cell.

### 2.4.2. Polarizing light microscopy (PLM)

A microscope (Olympus BX 51) equipped with a heating stage (Linkam THMSE 600) was used to observe the texture of samples during the heating and cooling processes. The samples kept between coverslips were heated from room temperature to  $150 \,^{\circ}$ C for double-chained quaternary ammonium salts, from room temperature to  $210 \,^{\circ}$ C for novel zwitterionic geminis. The samples were illuminated with linearly polarized light and analyzed through a crossed polarizer. To capture images at different temperatures, a video camera (Qimage 5.0 RTV) was used.

### 2.4.3. X-ray diffraction (XRD)

X-ray measurements of these samples were performed using Cu K $\alpha$  (1.542 Å) radiation monochromatized with a Rigaku D/MAX-rA X-ray diffractometer. The recording temperatures were chosen between points of phase transitions, in accordance with the DSC curves. Scanning rates in small-angle and wide-angle range were 4 and 2°/min, respectively.

### 3. Results and discussions

### 3.1. TGA and DSC results

Prior to study of thermotropic phase behaviors, the thermal stabilities of these double-chained quaternary ammonium chlorides have been analyzed systematically by thermogravimetry. All these compounds have similar thermal stability. They are found to decompose above temperature of 175 °C upon heating. A typical thermogram recorded for  $G_{12}A_{12}C$  is shown in Fig. 1. Upon heating, all these compounds are stable within the temperatures exhibiting thermotropic phase behaviors.

DSC is a useful tool, which complements optical methods in the study of liquid-crystalline phase transitions. To study the thermotropic mesophase formation in more detail, DSC studies on the synthesized compounds have been carried out. All transitions are endothermic in the heating cycle and exothermic in the cooling cycle for the nine compounds. Typical thermogram of  $G_{12}A_{12}C$  is illustrated in Fig. 2. On heating, these double-chained quaternary ammonium salts show two endothermic peaks, they correspond to the crystal–liquid crystalline ( $T_m$ ) and liquid crystalline-isotropic ( $T_i$ ) transition temperatures, respectively. On cooling, all these compounds show two exothermic peaks, they correspond to the isotropic-liquid crystalline ( $T_d$ ) and liquid crystalline-crystal ( $T_c$ ) transition temperatures, respectively [24,25]. All these compounds



Fig. 1. TGA trace of G<sub>12</sub>A<sub>12</sub>C registered in nitrogen upon heating at 10 °C/min.



Fig. 2. DSC thermogram of G<sub>12</sub>A<sub>12</sub>C during heating and cooling cycles.

exhibit enantiotropic behavior. The phase transition parameters, transition temperatures and changes in enthalpy, derived from the DSC heating and cooling scans of these compounds are summarized in Table 1.

Though the nine compounds show similar patterns of thermotropic phase behavior, there are some differences in the details. The increase in number of C-atoms in hydrocarbon chains of the double-chained quaternary ammonium chlorides leads to the decrease of the  $T_{\rm m}$ ,  $T_{\rm i}$ ,  $T_{\rm d}$ , and the increase of the  $T_{\rm c}$ . The temperature range for the occurrence of liquid-crystalline phase narrows with hydrocarbon chain length increase. It can be seen from Table 1 that  $G_{16}A_{16}C$  exhibits lower  $T_m$ ,  $T_i$ ,  $T_d$ , higher  $T_c$ , and narrower mesophase range than  $G_{12}A_{12}C$  and  $G_{14}A_{14}C$ . On the other hand, the symmetry in hydrocarbon chain length also influences the phase transition temperatures. The double-chained guaternary ammonium chlorides with higher degree of asymmetry in hydrocarbon chain length such as G<sub>16</sub>A<sub>12</sub>C and G<sub>12</sub>A<sub>16</sub>C display lower  $T_{\rm m}$  and  $T_{\rm i}$  in comparison with the more symmetrical compound G<sub>14</sub>A<sub>14</sub>C bearing the same total carbon numbers with the two former compounds.

As shown in Fig. 3, hysteresis phenomenon occurs for all the compounds when the clearing point is exceeded. The liquid crystalline crystal transition temperature shows more pronounced supercooling during cooling scan when compared to isotropic liquid crystalline transition temperature. For the nine double-chained quaternary ammonium chlorides, the  $T_c$  is shifted down

Table 1

Transition temperatures (*T*) and enthalpies ( $\Delta H$ ) of double-chained quaternary ammonium chlorides from DSC thermograms.

Compound	Heating		Cooling	
	T°C	$\Delta H (\mathrm{kJ}\mathrm{mol}^{-1})$	T°C	$\Delta H$ (kJ mol <sup>-1</sup> )
G <sub>12</sub> A <sub>12</sub> C	120.4	59.8	141.8	2.3
	145.5	2.3	85.5	53.7
$G_{14}A_{14}C$	120.0	68.1	139.2	1.6
	144.0	1.9	89.7	65.6
$G_{16}A_{16}C$	119.1	80.9	129.3	1.2
	136.0	1.7	92.2	80.8
G <sub>14</sub> A <sub>12</sub> C	118.0	58.1	139.6	2.0
	144.1	2.1	83.8	54.6
$G_{16}A_{12}C$	113.3	56.9	135.7	1.7
	141.0	1.9	81.6	58.6
$G_{12}A_{14}C$	120.7	64.4	143.1	2.0
	146.7	2.4	94.8	67.6
$G_{12}A_{16}C$	15.3	63.9	137.5	1.8
	142.6	1.9	84.9	62.0
G <sub>14</sub> A <sub>16</sub> C	116.3	62.6	133.9	1.3
	139.7	1.4	93.1	62.2
$G_{16}A_{14}C$	117.4	72.3	134.0	1.9
	139.8	1.8	88.7	71.8

for 34.9 ( $G_{12}A_{12}C$ ), 30.3 ( $G_{14}A_{14}C$ ), 26.9 ( $G_{16}A_{16}C$ ), 34.2 ( $G_{14}A_{12}C$ ), 32.2 ( $G_{16}A_{12}C$ ), 25.9 ( $G_{12}A_{14}C$ ), 30.4 ( $G_{12}A_{16}C$ ), 23.2 ( $G_{14}A_{16}C$ ), and 28.7 °C ( $G_{16}A_{14}C$ ), respectively. This result shows that as increasing the hydrocarbon chain length of these double-chained quaternary ammonium chlorides, they display a less pronounced thermal hysteresis in general.

As increasing hydrocarbon chain length for these doublechained quaternary ammonium chlorides, the enthalpies of the crystal-liquid crystalline phase transitions exhibits an increasing tendency in general (see Table 1). The melting enthalpy of G<sub>16</sub>A<sub>16</sub>C is the highest among the nine compounds. This is expected because the van der Waals interactions are stronger when the number of aliphatic carbons increases [11,23,26]. However, the enthalpy change per methylene group is not constant (not shown), but increases with hydrocarbon chain length, suggesting that molecules with longer hydrocarbon chain lengths give rise to more favorable packing arrangement. On the other hand, the higher asymmetry in hydrocarbon chain length induces lower melting enthalpy. The melting enthalpy of  $G_{16}A_{12}C$  and  $G_{12}A_{16}C$  is lower than that of G<sub>14</sub>A<sub>14</sub>C. It is also found from Table 1 that the enthalpy of liquid-crystalline phase isotropic transition is at 1.4-2.3 kJ/mol, which is relative small. Nematic and cholesteric liquid crystalline compounds usually exhibit small enthalpies of liquid-crystalline phase isotropic transition.

### 3.2. Microscopy results

The thermal phase behaviors of the nine compounds have been observed under polarized light microscope, between slide and cover slip. It has been found that all double-chain quaternary ammonium chlorides display similar textures and seems independent of the hydrocarbon chain length and symmetry. Thus, these pictures shown in Fig. 4 are representative. The microphotographs of the characteristic textures formed upon heating and cooling of these double-chained quaternary ammonium chlorides are illustrated in Fig. 4A–D. These characteristic textures observed for all the double-chained quaternary ammonium chlorides include oily-streak, schlieren, fan-shaped, and Maltese cross textures [12,27,28]. Oily streak texture (Fig. 4A) is apparent during heating, and a schlieren texture (Fig. 4B) is also observed in somewhere samples are relative thick.

When the isotropic state is cooled to deisotropic state, the fanshaped texture appears (see Fig. 4C). If a mechanical force is super-



**Fig. 4.** Optical micrographs of double-chained quaternary ammonium chlorides formed upon heating and cooling. (A) Oily-streak texture of  $G_{14}A_{12}C$  at 130 °C (upon heating,  $10\times$ ); (B) schlieren texture of  $G_{16}A_{12}C$  at 132 °C (upon heating,  $50\times$ ); (C) fan-shaped texture of  $G_{16}A_{16}C$  at 128 °C (upon cooling,  $20\times$ ); D maltese crosses of  $G_{16}A_{12}C$  at 128 °C (upon cooling,  $10\times$ ).

imposed on the sample, such as slightly shearing, the fan-shaped texture immediately transforms into oily-streak texture, which is typical of cholesteric liquid crystals [29]. Maltese crosses are also observed with thick samples during cooling. All the textures can well recur for repeating observation. Optical changes occur at temperatures in agreement with the DSC measurements for the nine compounds.

### 3.3. X-ray results

Further insight into the structural properties of mesophase for the double-chained quaternary ammonium chlorides is obtained



Fig. 3. Range of mesophase (shadow part) for double-chained quaternary ammonium chlorides upon heating (H) and cooling (C).



Fig. 5. XRD pattern of G<sub>12</sub>A<sub>12</sub>C at 130 °C upon heating.

by the examination of X-ray scattering data at mesophase transition temperature. It is found that all the double-chained quaternary ammonium salts exhibit similar packing arrangements of liquid-crystalline phases. Typically, the XRD pattern of all the quaternary ammonium chlorides in the liquid-crystalline phase consists of a broad, high-angle diffraction peak near  $2\theta = 20^{\circ}$ corresponding to the *intra*lamellar spacing as shown in Fig. 5 But, no diffraction peak is observed in small-angle region. Combining the results of PLM with XRD, it can be concluded that the double-chained quaternary ammonium chlorides form cholesteric liquid crystal [29,30].

### 4. Conclusion

Nine double-chained quaternary ammonium chlorides with symmetric and asymmetric hydrocarbon chain length, N-(3alkoxyl-2-hydroxy)propyl-N-alkyl dimethylammonium chloride  $R-O-CH_2-CH(OH)-CH_2-N^+(CH_3)_2-R\cdot Cl^-$  (R:  $C_{12}H_{25}$ ,  $C_{14}H_{29}$ ,  $C_{16}H_{33}$ ), have been synthesized and characterized by FT-IR, <sup>1</sup>H NMR, MS and elemental analysis. The thermotropic phase behaviors of these compounds have been investigated by DSC, PLM and XRD. The obtained results show that the hydrocarbon chain length and the symmetry in the hydrocarbon chain length of these compounds influence transition temperature, mesophase range, thermal hystersis, and enthalpy changes in some degree, but exhibit little effect on the class of liquid crystal. The longer hydrocarbon chain length of these compounds leads to lower  $T_{\rm m}$ , narrower mesophase range, weaker thermal hystersis, and higher melting enthalpy, and the higher asymmetry in the hydrocarbon chain length results in lower  $T_{\rm m}$  and melting enthalpy. In the temperature of mesophase range, all compounds show oily-streak, schlieren, fan-shaped and Maltese cross textures. XRD result shows that there is a sharp reflex in the small-angle region and a diffuse wide peak in the wide-angle region for all compounds. All these confirm that these compounds form cholesteric liquid crystal.

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.02.013.

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